UDC 666.1.022.8

EFFECT OF THE COMPONENT COMPOSITION AND OXIDATION – REDUCTION CHARACTERISTICS OF MIXES ON FOAMING OF PYROPLASTIC SILICATE PASTES

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Translated from *Steklo i Keramika*, No. 4, pp. 13 – 17, April, 2010.

The effect of the composition of mix based on different silica raw material and the oxidation-reduction characteristic of the components on the foaming process in obtaining foam-glass-crystalline materials is examined. It is established that foam-forming mixes belonging to the transitional oxidation-reduction group, whose oxidation coefficient lies in the range 25 – 100 are optimal for foaming. The oxidative and reducing mixes are characterized by a low foaming ratio and high degree of nonuniformity, which requires adjusting the composition by changing the ratio of the reducer oxidizer.

Key words: foam-glass-crystalline materials, mix, oxidation reduction characteristics, foaming.

The technology for foam glass materials, irrespective of the method used to obtain them and the type of foaming agent, includes the same operations, such as preparation and heat-treatment of the foaming medium, stabilization of the foam, and annealing. The strength, physico-chemical and thermophysical characteristics of the finished article largely depend on the porous structure formed in the process of foaming, the pore size, and the pore-size distribution. Some of the main factors affecting this stage are the redox processes proceeding with a change of the degree of oxidation of the elements participating in the foaming. The direction of the oxidation-reduction reactions is determined by the temperature regime used to process the mix, the composition of the gas medium, and the oxidation-reduction characteristic of the foaming mixture (Fig. 1). The dominant role in this process belongs to the composition of the foaming mixture in which a definite ratio of the oxidizers and reducers is formed. The effect of these factors on the process of obtaining foam-glass-crystalline materials has not been adequately studied. In contrast to foam glass, the latter are formed on the basis of abundant natural and technogenic raw materials by a low-temperature technology (< 900°C). Exclusion of glass-making at temperatures 1500°C makes it possible to lower the energy consumption and the cost of the final product.

The objective of the present work was to develop indicators that would make it possible to evaluate the effect of the composition of the initial mix based on different natural silica raw material and the oxidation-reduction characteristics (ORC) of its components on the foaming process in obtaining foam-glass-crystalline materials (FGCM).

In this work, glass-crystalline powder — granulated glass, consisting of a mixture of the product of low-temperature processing of the initial mix, and a foaming agent — grade 801 soot were used as the raw materials to obtain FGCM.

The driving force of the foaming process for a foam-glass mixture is the equality of the temperature of its pyroplastic state and the action foaming agent. Here the viscosity of the melt and the ratio of the amount of active oxidizers and reducers of the mixture which ensure gas release must be optimal. The main requirements for the properties of the granulated glass are presented in [1, 2], where it is shown that the viscosity of the granulated glass in the foaming temperature range (800 – 850°C) is in the range $10^5 – 10^8$ dPa · sec. The content of the residual crystalline phase of the granular glass, which depends on the composition of the initial mix, the nature of the glass-forming component, and the heat-treatment temperature, does not exceed 15% for silica compositions.

Silica materials such as marshallite, diatomite, and opoka are examined in this work. The component composition of the mix based on these materials and the phase composition of the granular glass obtained are presented in Table 1.

Indicators characterizing the interrelation of the composition, structure, and properties of material were used to evaluate the effect of the oxidation-reduction characteristic of the initial mixes on the process of obtaining and the quality of FGCM.

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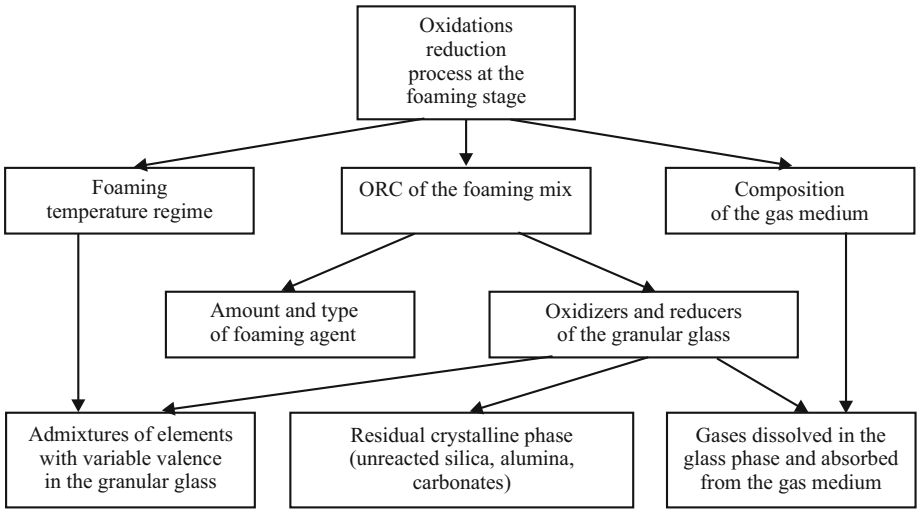

Fig. 1. Dependence of redox processes at the foaming stage on the main factors.

It is known that the transverse cross section of the barriers between pores has the main effect on the thermal conductivity of foam glass at low temperatures (< 300°C), while the radiation characteristics of the glass and the pore size have the main effect at high temperatures [3]. Thus the important structural indicators of a material are the pore size and the interpore barrier with a minimal variance of their values and uniformity of the distribution in the volume.

An indicator characterizing the degree of nonuniformity of the macrostructure is proposed as a characteristic of this structure:

$$C_{\text{non}} = \left| (C_{\max} m_{\text{l}} - C_{\min} m_{\text{s}}) / C_{\text{av}} m_{\text{c}} \right| \times 100, \qquad (1)$$

where $C_{\max}$ is the average size of the large pores, mm; $C_{\min}$ is the average size of the small pores, mm; C_{av} is the average size of the predominate pores, mm; and, m_{l}, m_{s}, and m_{c} are the numbers of large, small and predominant pores.

The average pore size is < 0.5 mm in the small pore structure, 1 – 3 mm in the average-pore structure, and > 3 mm in the large-pore structure. It was established that the FGCM samples with highly uniform structure are characterized by a degree of nonuniformity $C_{\text{non}} < 10\%$, and in medium and nonuniform structure with C_{non} is 11 – 20 and > 21%, respectively.

TABLE 1. Component and Phase Composition of the Mix and Granular Glass

Mix	Component content of the initial mix, wt.%			Content of the granular glass phases, wt.%	
	silica material	soda	dolomite	glass phase	crystalline
ShM-1	63 (marshallite)	30	7	99	1
ShM-2	63 (marshallite)	20	17	87	13
ShO-1	70 (opoka)	27	3	97	3
ShO-2	68 (opoka)	17	15	94	6
ShD-1	67 (diatomite)	27	6	86	14
ShD-2	66 (diatomite)	18	16	85	15

The results of numerous experiments have made it possible to propose a classification of FGCM according to the degree of their structural nonuniformity. Three types of structures were conditionally distinguished: small-pore with average pore size < 0.5 mm, medium- and large-pore 1 – 3 mm and > 3 mm, respectively. According to calculations, all FGCM can be divided according to the degree of structural nonuniformity into three groups:

with high uniform structure — $C_{\text{non}} < 10$;

with average degree of uniformity — $C_{\text{non}} = 11 - 20$;

with nonuniform structure — $C_{\text{non}} > 21$.

As practice has shown, the pore sizes in the FGCM samples obtained, depending on the foaming regime, vary over a wide range from 0.5 to 5 mm, and in some cases even larger. It was determined for the compositions studied that samples with a large-pore structure have a high degree of nonuniformity, while samples with 1 – 2 mm pores have the lowest degree of nonuniformity, and the most uniform structures are observed in them (Fig. 2).

The data of [4] show that the relative density of an article with cellular structure, the pore shape, and the barrier thickness are interrelated as follows:

$$\frac{\rho}{\rho_0} = 1 - \frac{K}{(1 + b/d)^3} \qquad (2)$$

according to which the pore structure coefficient is determined as

$$K = \left(1 - \frac{\rho}{\rho_0}\right)\left(1 + \frac{b}{d}\right)^3, \qquad (3)$$

where ρ is the density of the porous material, g/cm^3; ρ_{o} is the true density of the matrix (barrier body), g/cm^3; d is the cell

diameter, cm; b is the minimum thickness of a barrier, cm; and, K is the spore structure coefficient, showing the fraction of the maximum possible emptiness for a given barrier thickness.

The value of the coefficient varies from 0.52 (cubic packing of spherical voids) to 1 for a material consisting of cells in the form of polyhedra with the same barrier thickness. Thus, one must strive to obtain a material with coefficient equal to 1 in order to obtain a material with the lowest density. The s cells in foam glass that contain a gas phase can be spherical, but usually for low densities and high porosity the voids are polyhedral [5]. It is established in [6] that the structure of the pores in foam glass is close to hexagonal with inclusion of pores of different size. For average cell size 1.5 mm and foam glass material with density, for example, 198, 298, and 443 kg/m^3, the computed barrier sizes (for $K = 1$) are 42, 65, and 100 μm, respectively.

Thus, when the foaming process was investigated, not only the effect of the mix composition and oxidation-reduction characteristics of its components were evaluated but the possibility of obtaining materials with a uniform fine-pore structure with average pore size no more than 1.5 mm and density 180 – 300 kg/m^3 was also considered. The coefficient of effective foaming and the oxidation coefficient were proposed as comparative indicators characterizing the foaming of mixes with different compositions.

The coefficient of effective foaming K_V shows the degree to which the sample volume increases during heat-treatment when obtaining porous material with prescribed structural characteristics, specifically, with degree of nonuniformity no greater than 12 and with average pore and barrier sizes no more than 1.5 mm and 90 μm, respectively. To determine the coefficient K_V cylindrical samples (pressing pressure 1 MPa) 10 mm high and 10 mm in diameter, are prepared from the foaming mixture and then heat-treated in a tubular furnace at different temperatures, varying the maximum foaming and soaking temperatures. The optimal, from the standpoint of obtaining the macrostructure, conditions were found for each foaming mix and the value of the effective foaming coefficient was calculated for the sample:

$$K_V = (V_f - V_i)/V_i, \quad (4)$$

where V_f and V_i are the volume of the foamed and initial samples, mm^3.

This method makes it possible to determine relatively quickly the optimal foaming regime for a mix with a definite composition.

The foaming mixes studied were divided into three groups on the basis of the experimental results: high-foaming ($K_V \geq 8$), medium-foaming ($K_V = 4 – 7$), and low-foaming ($K_V < 4$).

The oxidation coefficient characterizes the quantitative ratio of the oxidizers and reducers in the foaming mixture and the initial glass mix, taking account of their content and the chemical oxygen requirement factor:

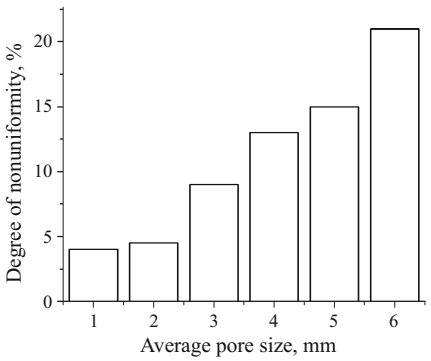

Fig. 2. Dependence of the degree of nonuniformity of FGCM on the average pore size.

$$K_o = (COR_f \times M_f + COR_o \times M_o)/(\sum COR_i \times M_i), \quad (5)$$

where COR_f, COR_o, and COR_i are the chemical oxygen requirement for 100 g of carbon-containing foaming agents, oxidizer, and the ith component of the initial mix, mg; M_f and M_o are the mass content of the foaming agent and oxidizer in the foaming mixture, %; M_i is the mass content of the ith component in the initial mix, %.

The COR of a material was determined using the standard method by means of the oxidation of the reducers in a mix with excess potassium bichromate followed by back-titration of its residue with a 0.1 N solution of Mohr's salt [7]. As the data in Table 2 show, the values of the COR of the mixes lie in the range 120 – 150 mg O_2 per 100 g of material, which corresponds to the range of values characteristic for colorless and green glass. The lowest value of COR among the silica materials studied is obtained for marshallite (125 mg O_2/100 g), and the highest value is obtained for opoka (166 mg O_2/100 g). Glass of the type KT (brown container) and SL (lamp), differing by the oxidation-reduction characteristics of the initial mixes, were used for comparative analysis. The values of COR of the mixes are 250 for KT and 125 mg O_2/100 g for SL.

It was shown for foaming mixtures differing by the value of COR of the initial mixes obtained with the addition of

TABLE 2. COR Values of the Materials and Mixes

COR of the raw materials, mg O_2/100 g of the material					
Soda	Dolomite	Diatomite	Marshallite	Opoka	Sodium sulfate
104	133	155	125	166	164
COR of the mixes, mg O_2/100 g of the mix					
ShM-1	ShM-2	ShO-1	ShO-2	ShD-1	ShD-2
119	122	148	150	140	142

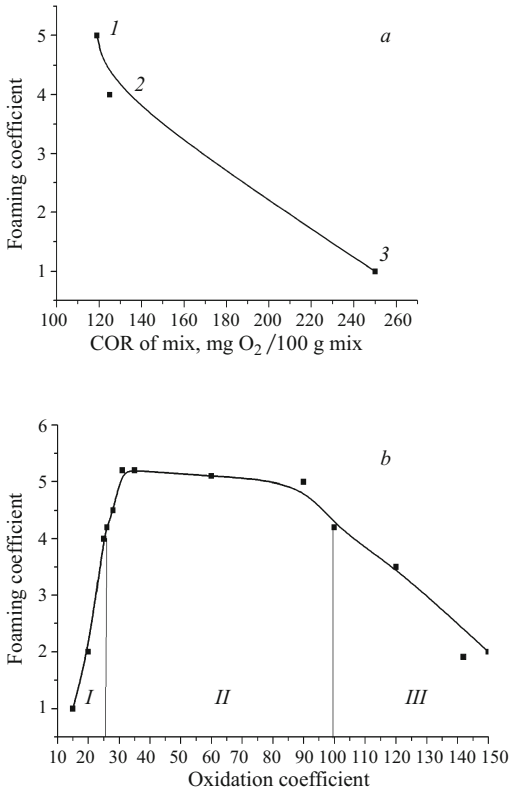

Fig. 3. Dependence of the foaming coefficient on COR of the initial mix (*a*) and the oxidizing coefficient of the foaming mixture (*b*): *1*) ShM-1 mix; *2*) mix for obtaining SL glass; *3*) mix for obtaining KT glass; *I*) oxidizing region; *II*) transitional region; *III*) reducing region.

0.5%[2] soot under identical foaming conditions (850°C, aging 15 min) that as the COR of the initial mix increases from 119 to 250 mg O_2/100 g the foaming coefficient decreases from 5 to 1 (Fig. 3*a*). As one can see from the date obtained, the foaming mixture based on brown container glass with 0.5% soot is a low-foaming composition, which indicates a deficiency of oxidizers in the mix.

To expand the range of values of the oxidation coefficient, standard mixes were prepared with the oxidizer Na_2SO_4 introduced into the foaming mixture and different content of soot (from 0.4 to 2.5%), whose COR value is 7730 mg O_2/100 g. The results of the experimentally obtained dependence of K_V on the oxidation coefficient, varying from 15 to 150, show that the foaming mixtures fall into three groups: oxidizing — $K_o < 25$, transitional (oxidation-reduction) — $25 < K_0 < 100$, and reducing — $K_o > 100$ (Fig. 3*b*).

It has been established that the foaming mixtures belonging to the transitional group are characterized by a uniform fine-pore structure, while for oxidizing and reducing groups a high degree of structural nonuniformity is observed (Table 3). All foaming mixtures obtained through the intermediate product — granular glass based on natural silica raw material — fall into the region of optimal values of K_o.

[2] Here and below — content by weight.

TABLE 3. Comparative Characteristics of the Foaming Process and Properties of Foam-Glass Materials

Mix*	K_o	K_V	C_{non}	Average pore size, mm	Average size of interpore barrier, μm		Average density of granule, kg/m^3
					experiment	calculation	
ShM-1	33	5.3	2	0.8	45	32	280
ShM-2	32	5.2	1	0.9	55	41	308
ShO-1	26	4.3	3	1.4	42	44	220
ShO-2	26	4.5	1	1.2	45	43	250
ShD-1	28	5.2	5	0.9	32	24	187
ShD-2	27	5.1	4	1.2	38	32	192
KT-1	15	1.0	23	1.5	180	149	620
KT-2	31	5.2	7	2.2	70	69	220
KT-3	34	4.9	5	1.9	75	83	300
KT-4	36	4.5	5	2.0	80	90	310
SL-1	24	3.8	15	1.5	90	109	574
SL-2	60	5.1	10	1.2	40	43	250
SL-3	90	5.0	12	2.0	45	50	180
SL-4	120	3.5	21	4.0	80	107	190
SL-5	150	2.0	25	5.0	105	274	370

* KT) brown container glass cullet; SL) lamp glass cullet.

For materials with a nonuniform structure ($C_{non} > 21\%$) the average sizes of the interpore barrier which were obtained experimentally and computed, differ substantially. The interpore barrier sizes for highly uniform structures agree quite well, which indicates that the relation (2) can be used for foam-glass-crystalline materials with a uniform pore distribution.

The structural nonuniformity of porous material could be due to a deficiency or excess of active oxidizer, which results in additional foaming reactions together with the main carbon oxidation reactions. The structural nonuniformity of materials obtained using mixes with a high oxidation coefficient (SL-4, SL-5) is determined by the sodium sulfate introduced into the mix, which as a component of the glass is reduced by carbon with formation of gases according to the reaction [8]:

$$\text{glass } SO_3 + 2C = \text{glass } S^{2-} + CO_2 + CO.$$

For mixes with a low oxidation coefficient (KT-1) the presence of iron in the glass has a large effect, since the intensity of the brown color of glass is directly proportional to the product of S^{2-} and Fe^{3+}. The following reactions, leading to gas formation, are possible with the participation of iron oxide:

$$3CO + Fe_2O_3 = 3CO_2 + 2\,FeO;$$

$$FeO + CO = Fe + CO_2;$$

$$FeO + C = Fe + CO.$$

Since iron is one of the most abundant elements with variable valence present in natural raw materials, this must be taken into account when determining FGCM.

Analysis of the data obtained permits drawing the following conclusions:

the crystalline phase of granular glass, in amounts up to 15%, does not have a negative effect on foaming when obtaining foam-glass-crystalline materials; all foaming mixes obtained on the basis of granular glass belong to the group of medium-foaming materials with foaming coefficient greater than 4;

foaming mixtures whose oxidation coefficient lies in the range 25 – 100, i.e., they belong to the transitional oxidation-reduction group, are optimal for foaming;

the oxidation and reduction foaming mixtures — $K_o < 25$ and $K_o > 100$, respectively — are characterized by a low foaming coefficient $K_V < 3$ and a high degree of nonuniformity, which requires adjusting the composition by changing the ratio of the reducing and oxidizing agents;

the macrostructure of the foam-glass-crystalline samples obtained through granular glass based on silica raw materials is characterized by a high degree of uniformity ($C_{non} < 10\%$) and optimal pore and interpore barrier sizes (no greater than 1.4 mm and 60 μm), which makes it possible to obtain materials with density 190 – 300 kg/m^3.

This work was supported by RFFI Grant No. 09-03-12053-ofm_m and European Commission Grant No. 228536 (NMP4-SL-2009-228536 as part of the NEPHH project.

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